The Stability of Base-metal Thermocouples in Air from 800 to 2200 °F.

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I. Introduction

With the widespread use of base-metal thermocouples for temperature measurement and control in industrial processes there are numerous instances where high accuracy is of vital importance. Some processes require that a given temperature be maintained within narrow limits for an extended period of time if efficiency in operation and uniformity in production are to be maintained. In order to meet these requirements a more complete knowledge of the thermoelectric stability of base-metal thermocouple materials is necessary.

Practically all base-metal thermocouple wire produced in this country is annealed or given a stabilizing heat treatment by the manufacturer. For most purposes this treatment renders the product sufficiently stable so that further changes which may occur while the thermocouple is in service may be neglected. However, when high accuracy is required throughout the useful life of the thermocouple, these changes must be taken into account. In many industrial processes, thermocouples, when placed in service, are left undisturbed until there is evidence of either mechanical failure or serious error in the temperatures indicated. However, long before this occurs, the thermocouple may have changed to such an extent as to make it unreliable for accurate temperature measurement. The changes in the thermoelectric characteristics of thermocouple materials due to ordinary service conditions are usually gradual and cumulative. They depend upon such factors as the temperatures encountered, the length of time in service, and the atmosphere surrounding the thermocouple. The various types of thermocouple materials are affected in various ways and to various degrees.

When the reference-junction temperature is maintained constant, the emf developed by a homogeneous thermocouple depends only on the temperature of the measuring junction. The emf developed by an inhomogeneous thermocouple depends not only on the temperature of the measuring junction but also on the temperature distribution throughout the inhomogeneous portions of the wires. All base-metal thermocouples become inhomogeneous with use at high temperatures. However, if all the inhomogeneous portions of the thermocouple wires are in a region of uniform temperature, the inhomogeneous portions have no effect upon the indications of the thermocouple. Therefore, an increase in the depth of immersion of a used couple has the effect of bringing previously unheated portions of the wires into the region of temperature gradient, and thus the indications of the thermocouple will correspond to the original emf-temperature relation, provided the increase in immersion is sufficient to bring all the previously heated part of the wires within the zone of uniform temperature. If the immersion is decreased, the more inhomogeneous portions of the wires will be brought into the region of temperature gradient, thus giving rise to a change in the indicated emf. Furthermore, a change in the temperature distribution along inhomogeneous portions of the wire nearly always occurs when a couple is removed from one installation and

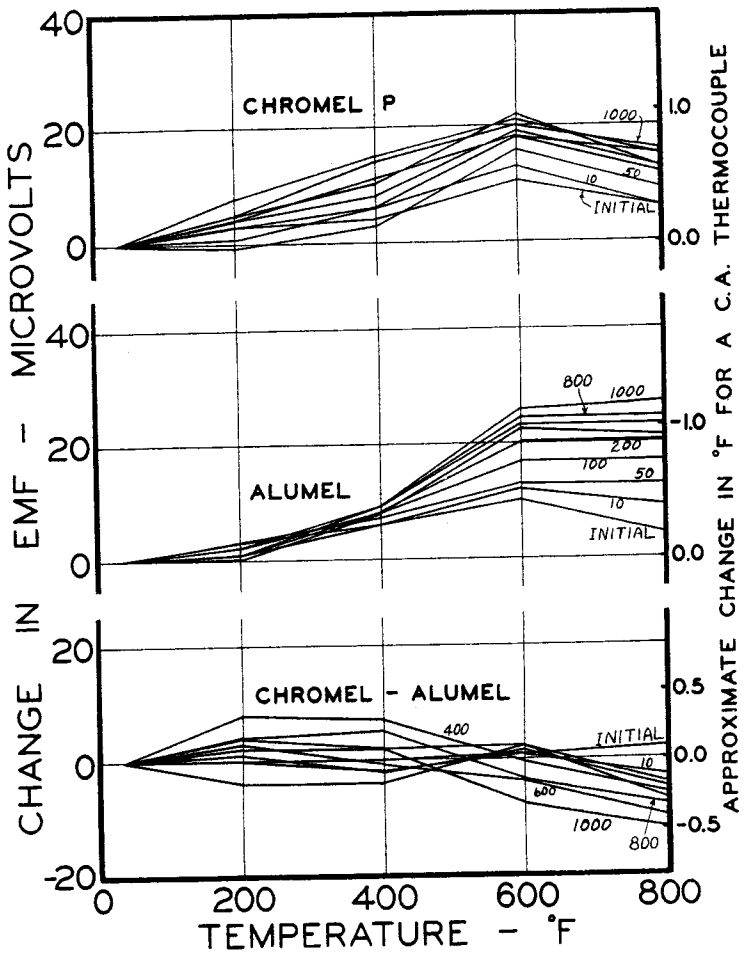

FIG. 1. Changes in No. 18-gage Chromel P and Alumel due to heating in air at 800 °F for the total times indicated on the graphs.

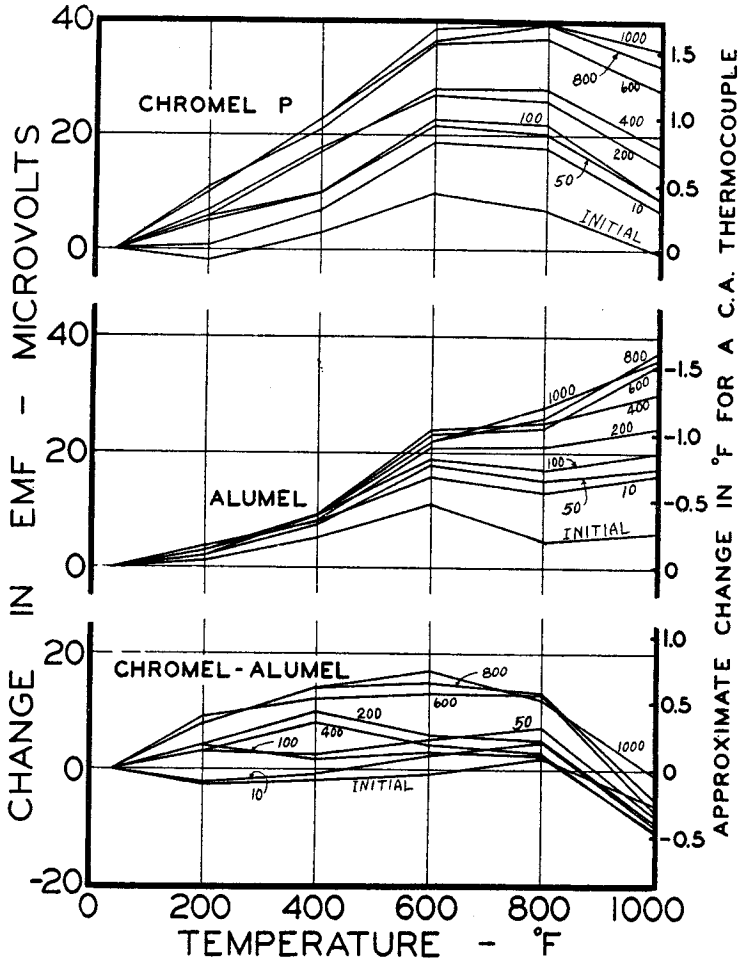

FIG. 2. Changes in No. 18-gage Chromel P and Alumel due to heating in air at 1000 °F for the total times indicated on the graphs.

placed in another, even though the measured immersion and the temperature of the measuring junction are the same in both cases. Thus the indicated emf is changed.

Although it is recognized that there are differences in composition and thermoelectric properties between various lots of thermocouple materials of the same general type, it is believed that the changes in the thermoelectric properties of a few selected lots of material will give a general idea of the changes which would occur in other lots of the same general type, providing that all lots have received the same initial heat treatment.

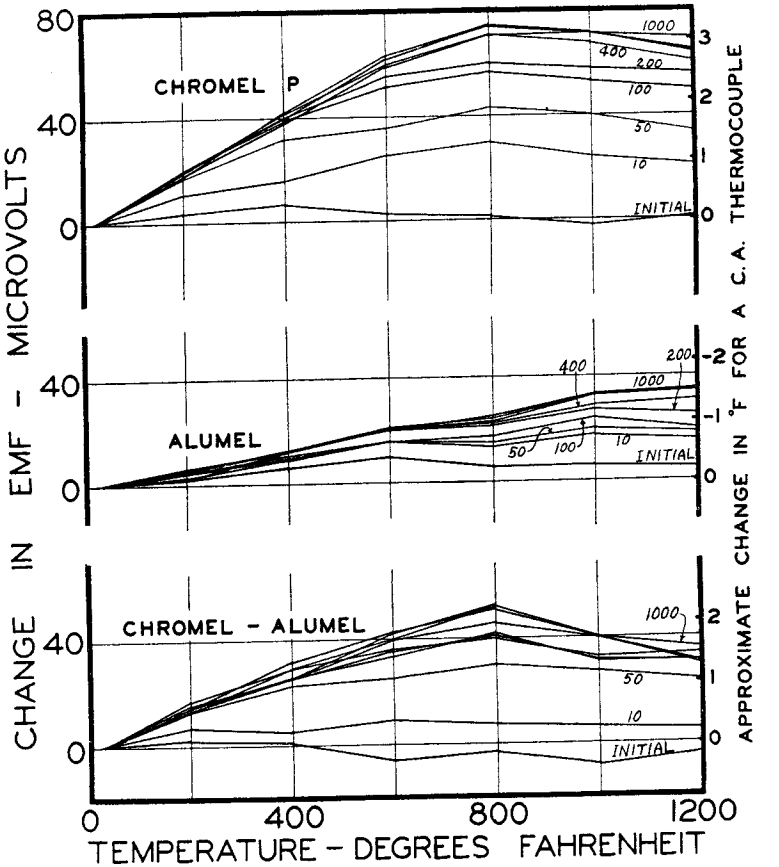

FIG. 3. Changes in No. 8-gage Chromel P and Alumel due to heating in air at 1200 °F for the total times indicated on the graphs.

II. Materials Investigated

The thermocouple materials studied were Chromel P, Alumel, iron, and constantan. Chromel P and Alumel wire of No. 18 gage, and iron and constantan of No. 14 gage were used for the tests at 800 and 1000 °F. For the test at 1200 °F and above, No. 8-gage wires were used. To determine the relation of wire size to the thermoelectric stability, additional tests were made on No. 18- and No.

22-gage Chromel P and Alumel at 1200 and 1600 °F, and on No. 18-gage iron and constantan at 1200 and 1400 °F.

Samples of the various materials were secured from several sources. Each of the materials used in the investigation had the temperature-emf relation characteristic of the large percentage of the material of its particular type now being manufactured. All the wires had been heat-treated by the manufacturers in the manner considered standard for the particular type of wire.

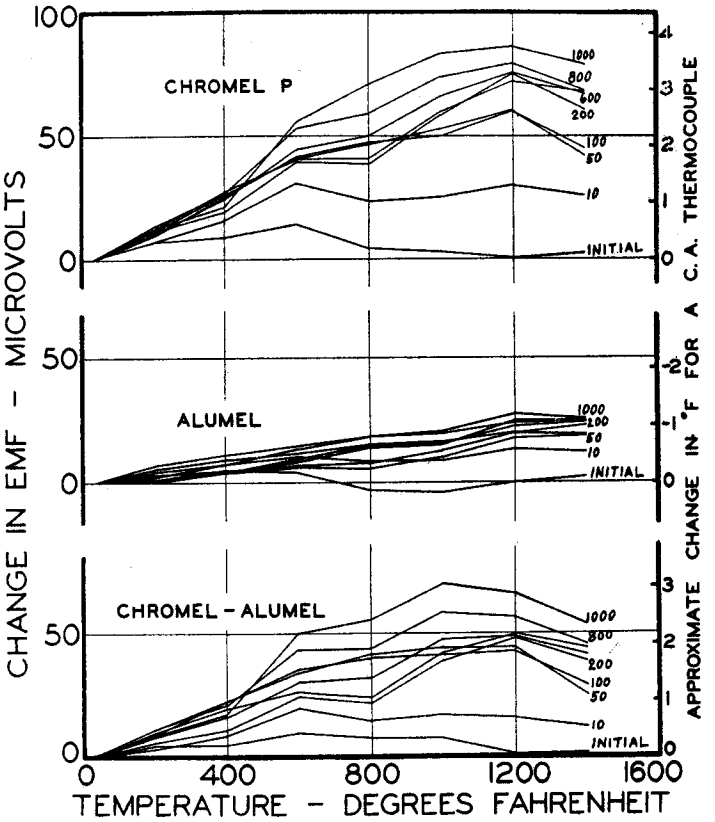

FIG. 4. Changes in No. 8-gage Chromel P and Alumel due to heating in air at 1400 °F for the total times indicated on the graphs.

III. Test Methods

Since Chromel P is generally used in combination with Alumel, and iron with constantan, the materials were paired in this manner. In addition to determining the temperature-emf relation for each pair, the thermal emf of the individual elements of each pair against the platinum standard,[1] Pt 27, was determined. In this way the thermoelectric changes of each thermocouple material were determined independently. The difference of the thermal emfs of the individual elements of a thermocouple against a third material is equal to the emf of the thermocouple. As all three were measured in this work, any two served as a check upon the third.

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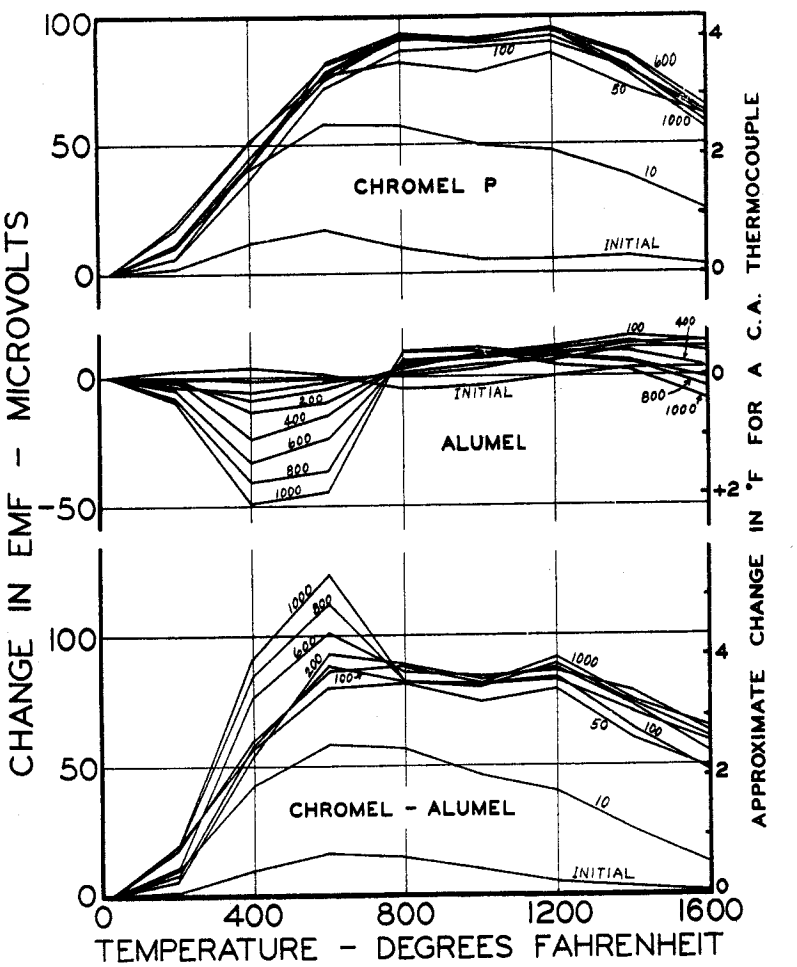

FIG. 5. Changes in No. 8-gage Chromel P and Alumel due to heating in air at 1600 °F for the total times indicated on the graphs.

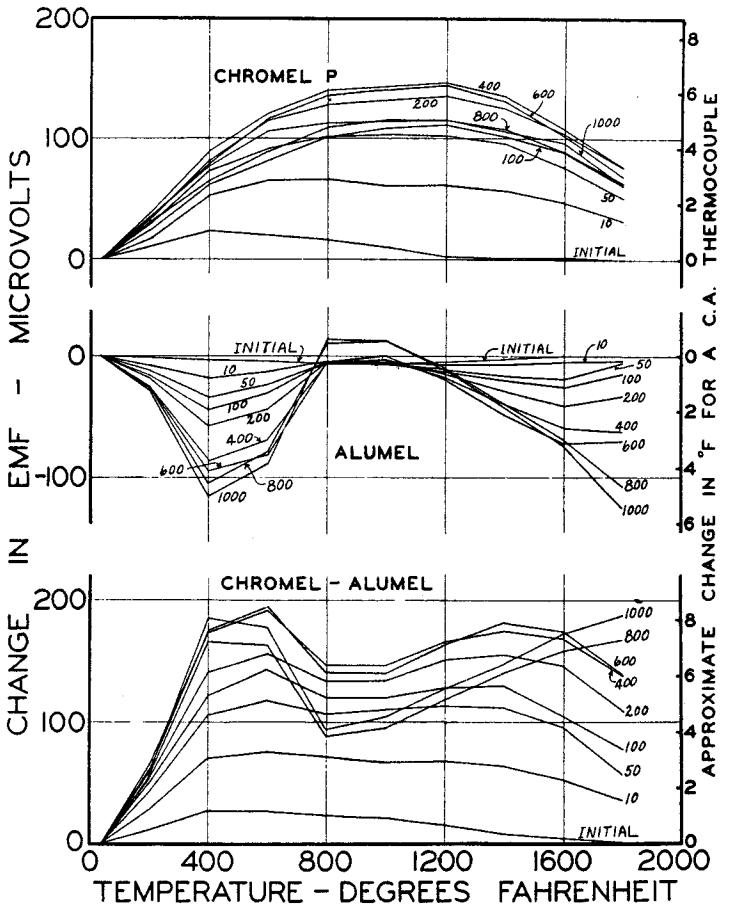

FIG. 6. Changes in No. 8-gage Chromel P and Alumel due to heating in air at 1800 °F for the total times indicated on the graphs.

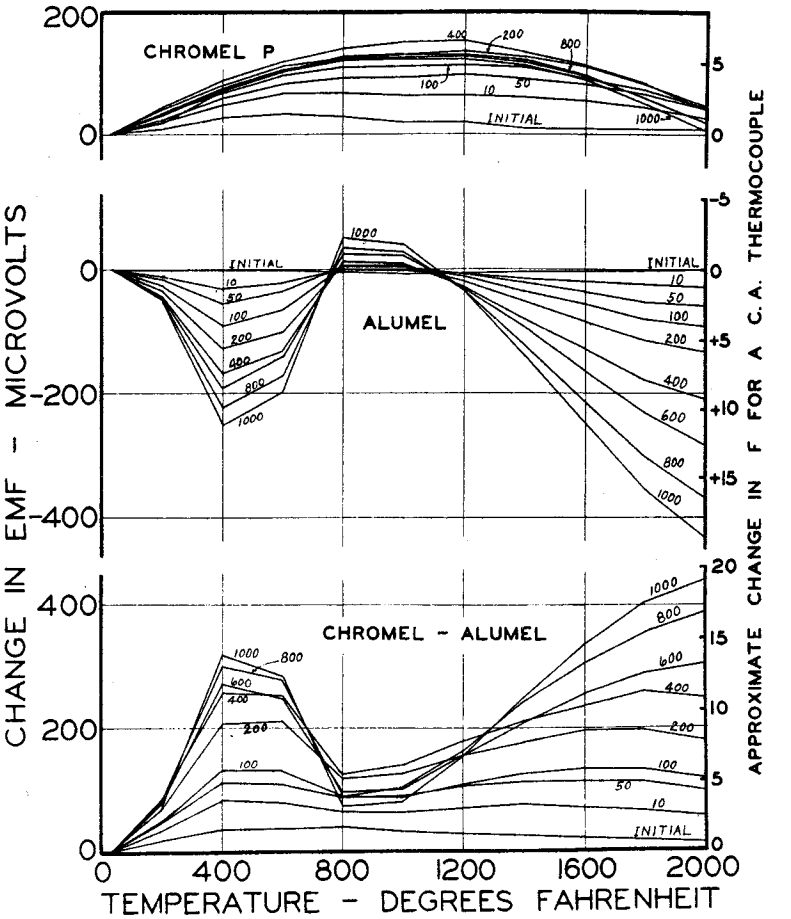

FIG. 7. Changes in No. 8-gage Chromel P and Alumel due to heating in air at 2000 °F for the total times indicated on the graphs.

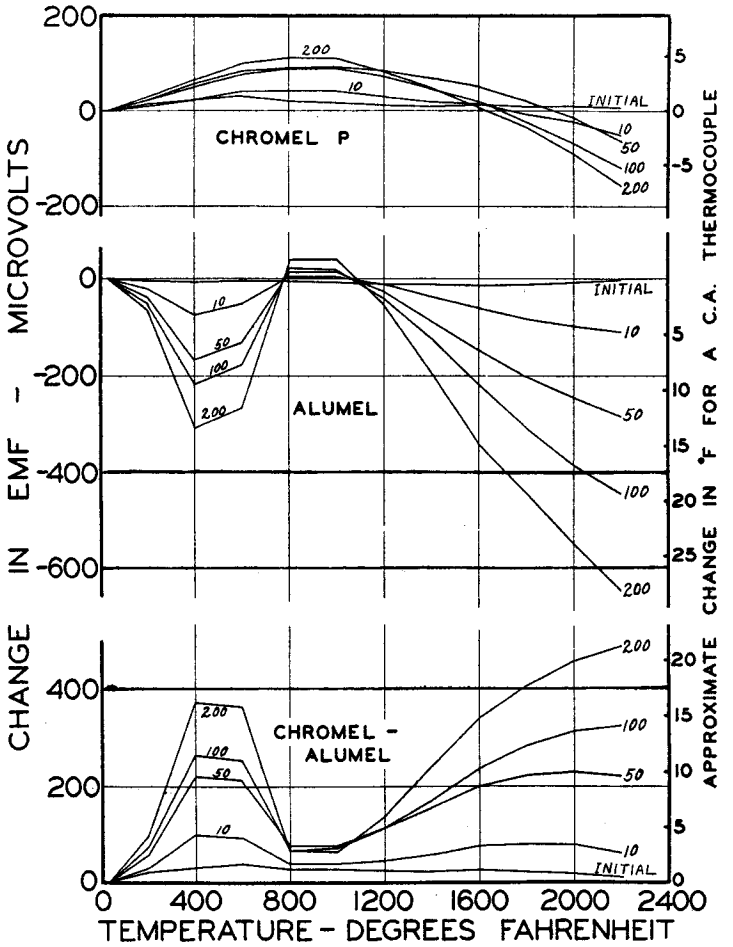

FIG. 8. Changes in No. 8-gage Chromel P and Alumel due to heating in air at 2200 °F for the total times indicated on the graphs.

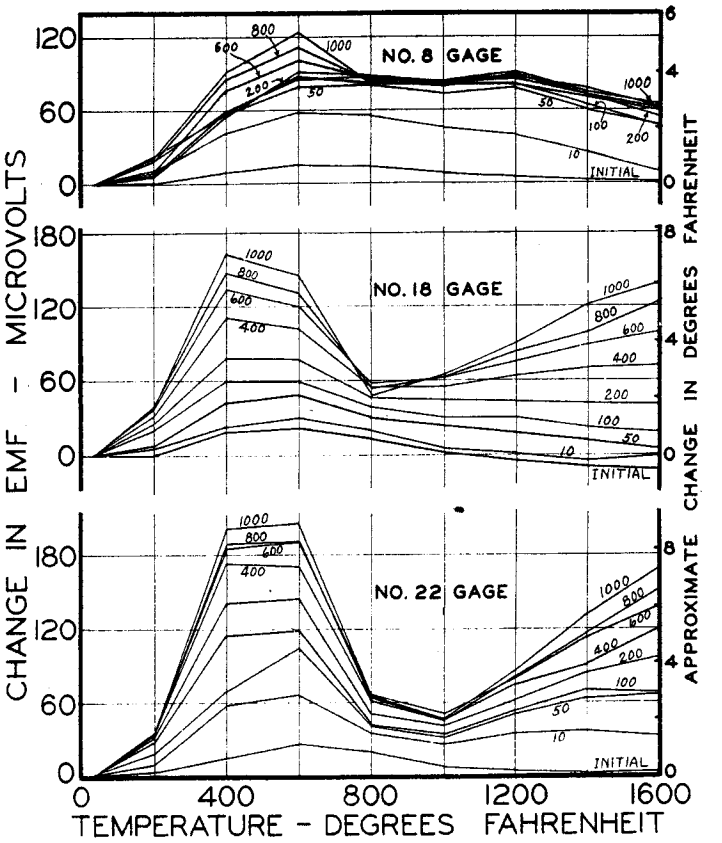

FIG. 9. Changes in No. 8, No. 18, and No. 22-gage Chromel-Alumel thermocouples due to heating in air at 1600 °F for the total times indicated on the graphs.

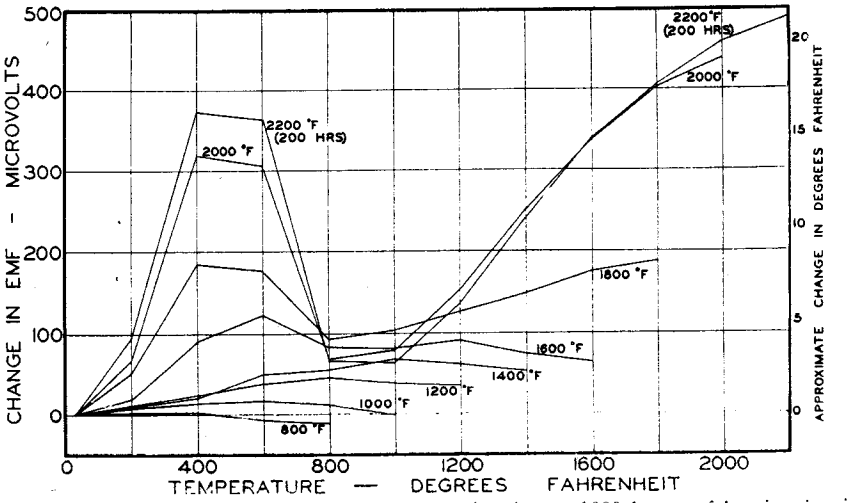

FIG. 10. Changes in Chromel-Alumel thermocouples due to 1000 hours of heating in air at temperatures indicated on the graphs.

The temperatures were measured with a standard platinum to platinum-10 per cent rhodium thermocouple calibrated in accordance with the specifications for the International Temperature Scale.[2] The platinum working standard used was checked periodically against Pt 27.

The pair or pairs of wire under test were insulated by 2-hole porcelain insulators. The platinum reference wire was protected by a glazed porcelain tube and

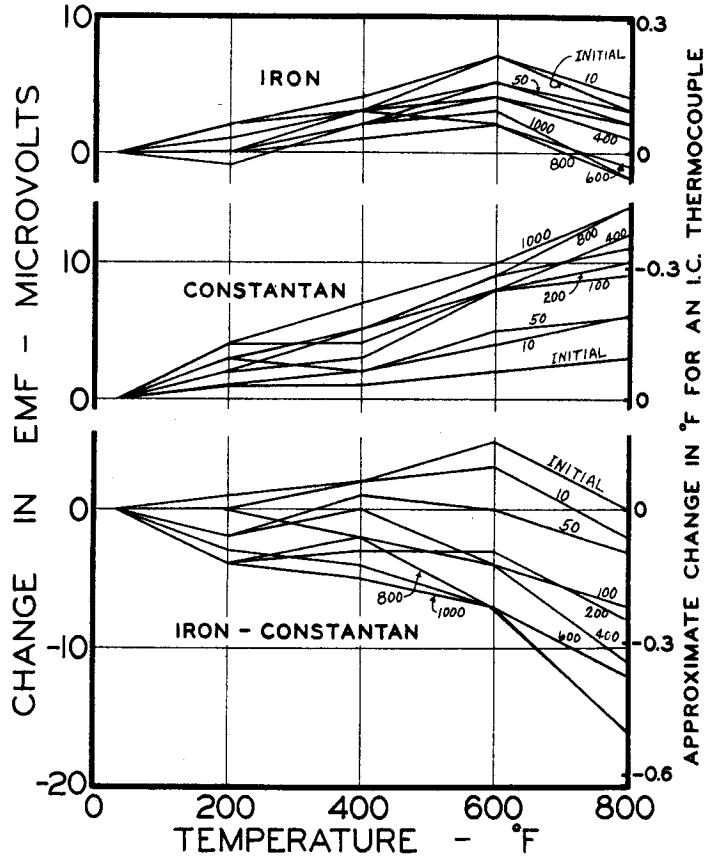

FIG. 11. Changes in No. 14-gage iron and constantan due to heating in air at 800 °F for the total times indicated on the graphs.

was sealed through the end of the protection tube with a "Pyrex" glass, leaving about 1 cm of the end of the wire protruding beyond the seal. The platinum-rhodium thermocouple, insulated with a 2-hole porcelain tube inside a glazed porcelain protection tube, was likewise sealed through the end of its protection tube with a "Pyrex" glass, leaving the welded junction protruding about 1 cm beyond the seal. The ends of the base metal wires, the platinum reference wire and the standard thermocouple were then welded together to form a single composite junction.

The furnace used in this work was of the resistance type wound with platinum-

rhodium wire. The furnace tube of Alundum was 60 cm long and 3 cm inside diameter. The wires under test, together with the platinum reference wire and the platinum-rhodium thermocouple, were placed in the furnace with the composite junction at about the midpoint. The wires were then securely clamped with respect to the furnace. Although the ends of the furnace tube were closed with asbestos wool to promote temperature uniformity, no attempt was made to exclude air from

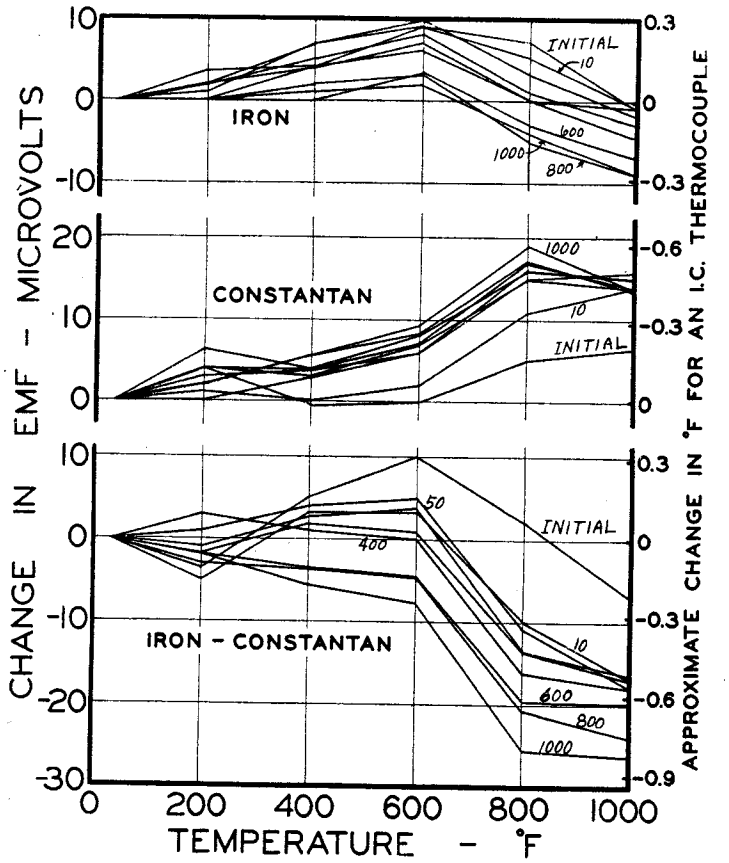

FIG. 12. Changes in No. 14-gage iron and constantan due to heating in air at 1000 °F for the total times indicated on the graphs.

the heated chamber, so that the atmosphere prevailing within the tube was oxidizing. The reference junctions were maintained at 32 °F during all the measurements. The temperature of the furnace was maintained practically constant during any observation at a given point by means of a hand-operated voltage regulator in the power circuit.

To obtain data on the effect of long-time exposure to high temperatures upon the thermoelectric properties of the materials the following procedure was adopted. The initial measurements were made on the sample as received from the manufacturer. Measurements of the thermal emfs of the various combinations were made

at intervals of 200 °F, up to and including in each case the temperature at which the effect of heating was to be determined. The furnace was then allowed to cool to room temperature and the measurements repeated. The differences between the two sets of measurements were ascribed to the initial heating and will be referred to as the "initial changes." Similar measurements were then made after the materials had been held at the test temperature for total elapsed times of 10, 50, 100, 200, 400, 600, 800, and 1000 hours, or as long as the materials remained service-

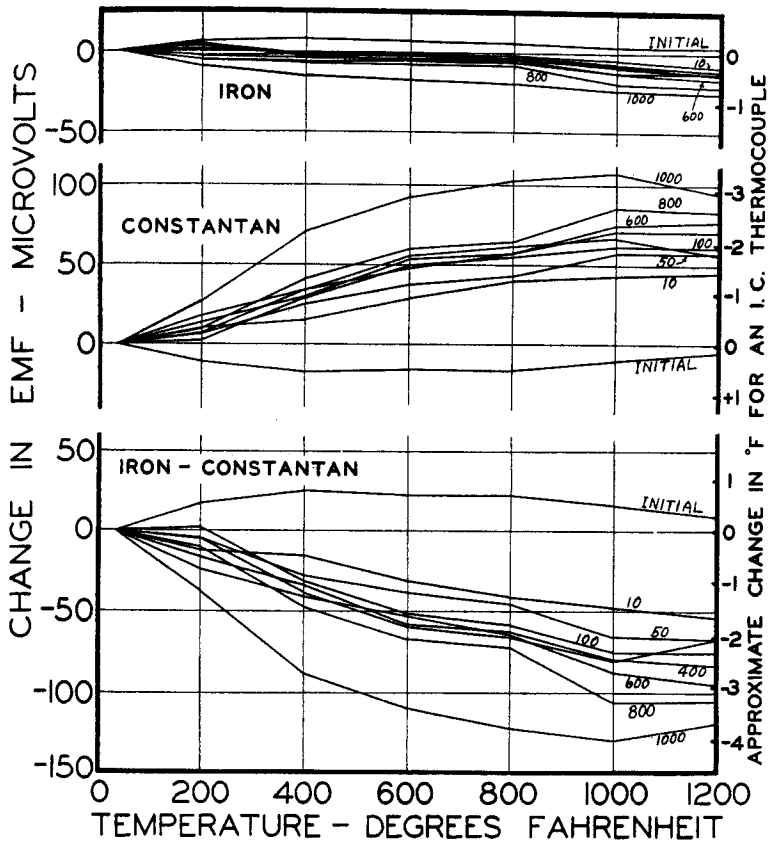

FIG. 13. Changes in No. 8-gage iron and constantan due to heating in air at 1200 °F for the total times indicated on the graphs.

able. The test temperatures included every temperature from 800 °F to and including 2000 °F in steps of 200 °F. Chromel P and Alumel were also tested at 2200 °F. A fresh sample was used for the test at each temperature. During heating periods the temperature of the furnace was maintained constant within ±5 °F by means of an automatic temperature controller.

The procedure followed in studying the effect of decreasing the depth of immersion was as follows. The materials were heated in the electric furnace for a period of 20 hours at a constant temperature. Following this heat treatment the thermal

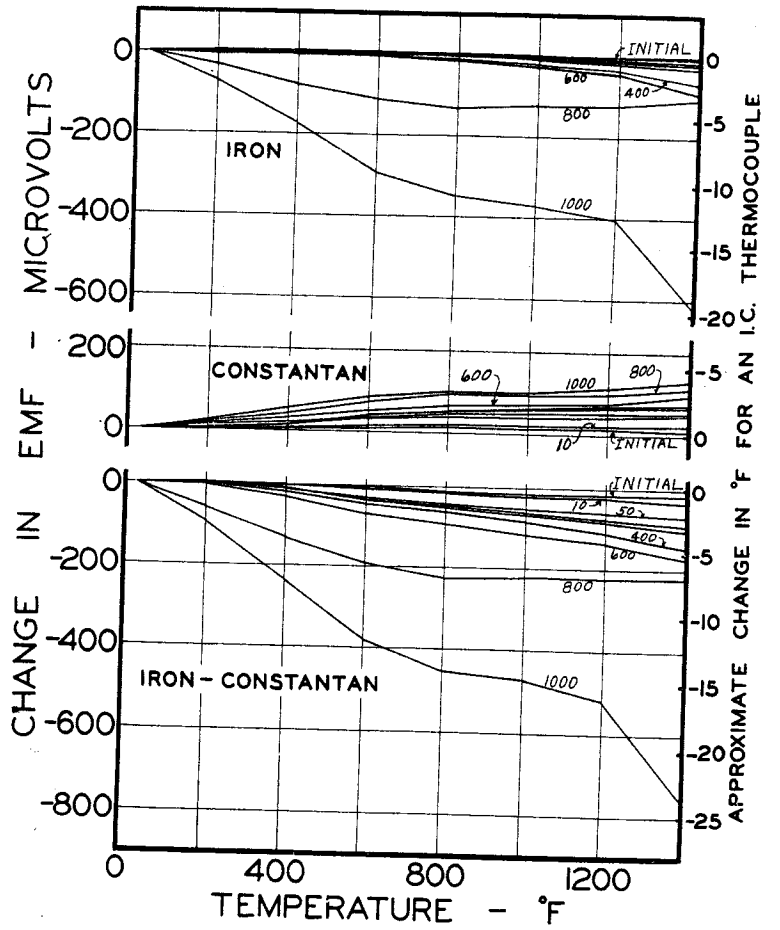

FIG. 14. Changes in No. 8-gage iron and constantan due to heating in air at 1400 °F for the total times indicated on the graphs.

emf of the samples was determined, the position of the samples being maintained the same as that during the 20-hour heating period. The furnace was then allowed to cool to room temperature, the immersion was decreased 3 inches, and the thermal emfs were determined in this new position. The difference between the observations for a given sample is due only to the change in immersion, since no heating took place between the two sets of measurements. This type of test was carried out on No. 8-gage iron and constantan at temperatures from 600 to 1800 °F in 200 °F steps and on No. 8-gage Chromel P and Alumel from 600 to 2200 °F.

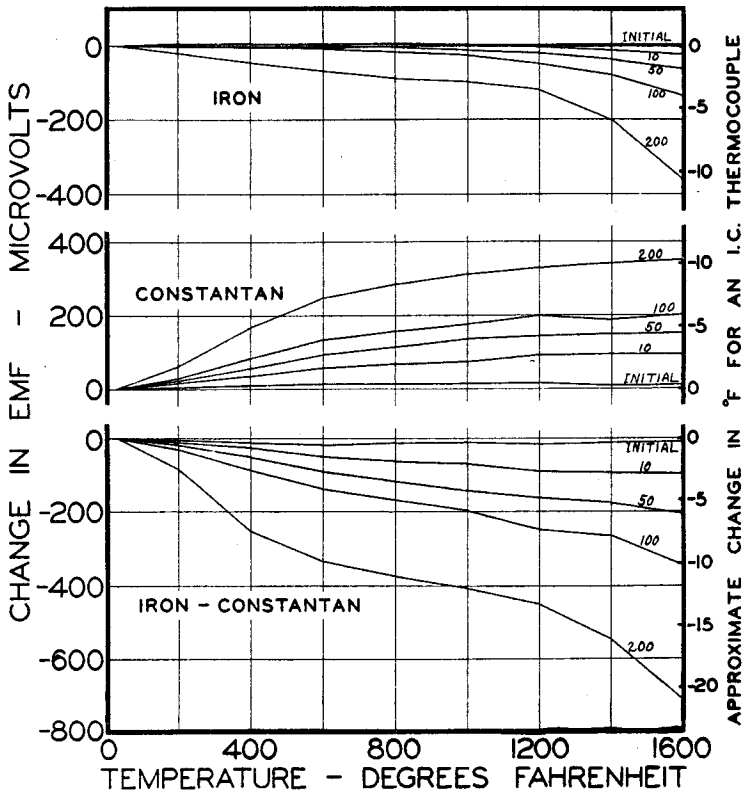

FIG. 15. Changes in No. 8-gage iron and constantan due to heating in air at 1600 °F for the total times indicated on the graphs.

IV. Results

A. Temperature Exposure Tests

1. Chromel P and Alumel. Figs. 1 and 2 show the results obtained on No. 18-gage Chromel P and Alumel heated at 800 and 1000 °F, respectively. The changes in the completed Chromel-Alumel thermocouples are also shown. The changes in the individual elements are in the same direction, so that each becomes thermoelectrically positive to the material in its original condition. The convention followed in regard to sign is as follows. If in a simple thermoelectric circuit

the current flows from metal A to metal B at the colder junction, A is thermoelectrically positive to B. On the basis of this convention Chromel P is positive to Alumel. Therefore a positive change in Chromel P will increase the emf of a Chromel-Alumel thermocouple, whereas a positive change in Alumel will decrease the emf of the thermocouple. The changes observed in the tests at 800 and 1000 °F are small, in all cases less than the equivalent of 1 °F for a Chromel-Alumel thermocouple.

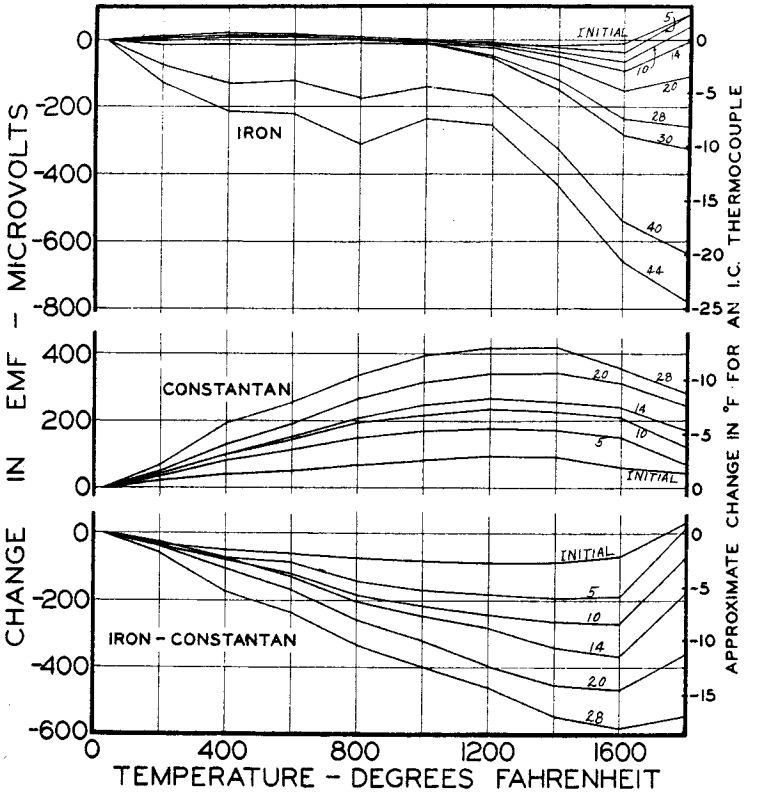

FIG. 16. Changes in No. 8-gage iron and constantan due to heating in air at 1800 °F for the total times indicated on the graphs.

Figs. 3 to 8 inclusive show the results obtained with No. 8-gage Chromel P and Alumel at temperatures from 1200 to 2200 °F inclusive. The changes in the emf of Chromel P are in the positive direction throughout all tests with the exception of the test at 2200 °F where a negative change was observed at temperatures above 1600 °F. The magnitude of the changes is in nearly all cases in the order of the duration of the heating periods, the maximum change occurring at about 1200 °F. The changes in the Alumel are in the positive direction throughout the tests at 1200 and 1400 °F. In the tests at 1600 °F and above, the changes in the emf of the Alumel between about 800 and 1100 °F are extremely small. Above 1100 °F the changes are negative and of appreciable magnitude. This is most

clearly shown in Fig. 7. The materials used in the test at 2200 °F failed after about 300 hours of heating.

Tests of No. 8-, No. 18-, and No. 22-gage Chromel-Alumel thermocouples heated at 1200 °F for a total of 1000 hours indicated that the changes in the thermocouples of the various sizes were nearly the same and in all cases less than the equivalent of 2.5 °F. Fig. 9 shows the effects on the same sizes of Chromel-Alumel thermocouples when heated at 1600 °F. The change in calibration at 400 °F is largest in the smallest size, but the reverse is true for the change at 1000 °F.

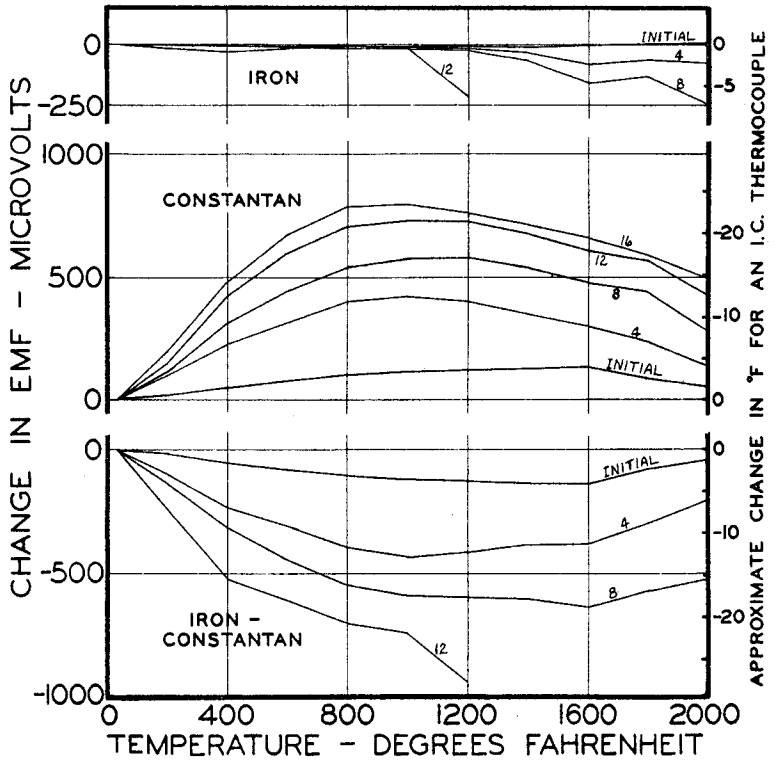

FIG. 17. Changes in No. 8-gage iron and constantan due to heating in air at 2000 °F for the total times indicated on the graphs.

The changes in the emf of the Chromel-Alumel thermocouples produced by the total heating time in each of the tests are shown in Fig. 10 (reproduced from Figs. 1 to 8, inclusive). In the test at 2200 °F the change after only 200 hours is shown, this being the elapsed time when the last measurements preceding failure were made. The peculiar change in the Alumel previously mentioned is reflected in change of the thermocouples.

2. Iron and Constantan. Figs. 11 and 12 show the results obtained on No. 14-gage iron and constantan tested at 800 and 1000 °F, respectively. The changes in all cases are small, being less than the equivalent of 1 °F.

The results on No. 8-gage iron and constantan tested at 1200 to 2000 °F inclusive are shown in Figs. 13 to 17. The time intervals between calibrations were shortened for the tests at 1800 and 2000 °F since at these temperatures the materials change at a rapid rate. The tests were continued until the materials failed.

The relative thermoelectric stability of No. 8- and No. 18-gage iron-constantan thermocouples heated at 1400 °F is shown in Fig. 18. As might be expected, the emf changes in the smaller wire proceed more rapidly. The No. 18-gage thermocouple failed after about 400 hours of heating, whereas the No. 8-gage remained

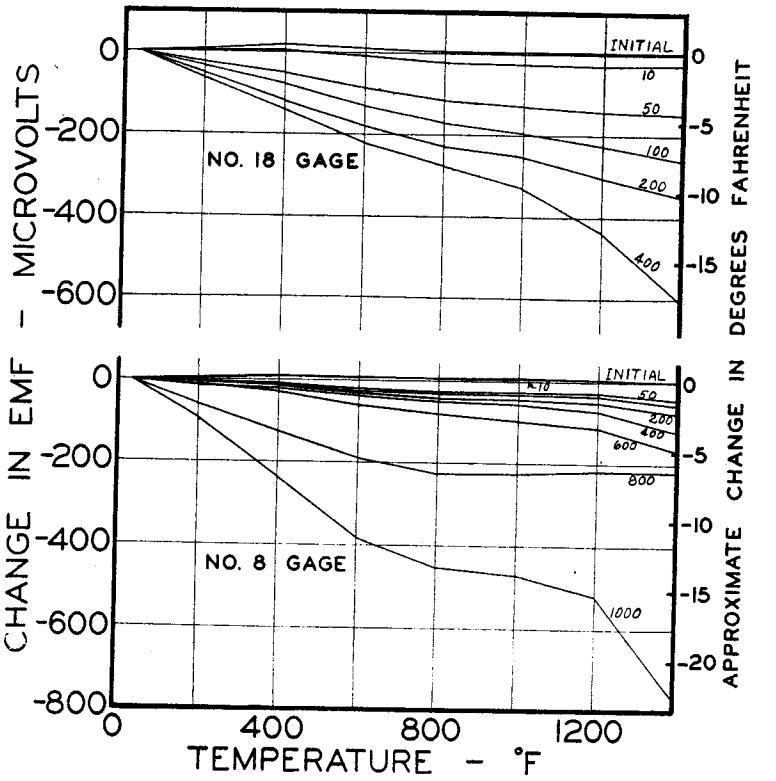

FIG. 18. Changes in No. 8 and No. 18-gage iron-constantan thermocouples due to heating in air at 1400 °F for the total times indicated on the graphs.

serviceable throughout the 1000 hours of the test. However, the measurements made on the thermocouple at the end of the 1000-hour period indicated that failure was near. A test on these same sizes at 1200 °F showed no appreciable difference in their thermoelectric stability at this test temperature, the maximum change after 1000 hours of heating being about the equivalent of 4 °F.

The change in the emf of constantan was gradual and cumulative throughout each test. In the case of iron, the change in emf was relatively small until failure of the wire was approached. When this stage was reached, the change was rapid and relatively large. This was true for all tests in which iron was heated until

failure. The life of the iron element was found to be approximately the same as that of the constantan.

B. Immersion Tests

Table 1 gives the observed changes in the thermal emf of No. 8-gage iron and constantan produced by a 3-inch decrease in immersion following the 20-hour heating period. The changes in both of the elements are gradual and regular throughout, the magnitude of the emf changes in constantan being everywhere considerably greater than in the case of iron. Fig. 19 shows the change in the emf of the iron-constantan thermocouple under the various conditions of heating (test at 1800 °F not shown in graph). A greatly increased, though regular, change is clearly shown for the test at 1600 °F. At 1800 °F the change is about 4 times as great as that observed at 1600 °F.

Table 1. Changes (in microvolts) at Various Temperatures Caused by Decreasing the Depth of Immersion Three Inches after Heating in Air at the Temperatures Indicated for 20 Hours.

Calibration Temp. (°F)	Heating Temperature (°F) 600	800	1000	1200	1400	1600	1800
				Iron			
200	1	5	3	1	− 2	− 1	− 2
400	0	7	4	3	− 2	− 4	− 9
600	1	8	3	4	− 2	− 7	− 18
800		7	2	4	− 3	− 12	− 29
1000			3	4	− 6	− 19	− 43
1200				1	− 9	− 30	− 58
1400					− 13	− 43	− 72
1600						− 57	− 80
1800							− 100
				Constantan			
200	4	10	13	14	14	25	83
400	7	18	20	30	28	62	224
600	9	27	26	43	41	93	374
800		35	37	52	53	127	504
1000			49	60	54	156	615
1200				65	65	182	735
1400					68	208	837
1600						223	935
1800							1078
				Iron-Constantan			
200	− 3	− 5	− 10	− 13	− 16	− 26	− 85
400	− 7	− 11	− 16	− 27	− 30	− 66	− 233
600	− 8	− 19	− 23	− 39	− 43	− 100	− 392
800		− 28	− 35	− 48	− 56	− 139	− 533
1000			− 46	− 56	− 60	− 175	− 658
1200				− 64	− 74	− 212	− 793
1400					− 81	− 251	− 909
1600						− 280	− 1015
1800							− 1178

Table 2 gives the observed effects for No. 8-gage Chromel P and Alumel of changes in immersion as outlined above. In the tests up to and including 1600 °F the effect is gradual and approximately regular. At 1800 °F and above the Alumel element exhibited an irregular effect, somewhat similar to that observed in the exposure tests, which became more pronounced as the heating temperature was increased. Fig. 20 illustrates the results for the Chromel-Alumel thermocouples.

V. Discussion of Results

As has been previously pointed out the materials were heated in an atmosphere of clean air. Furthermore, the depth of immersion of the materials in the furnace was constant throughout each exposure test. Direct application of the results obtained must be limited to cases where these conditions prevail.

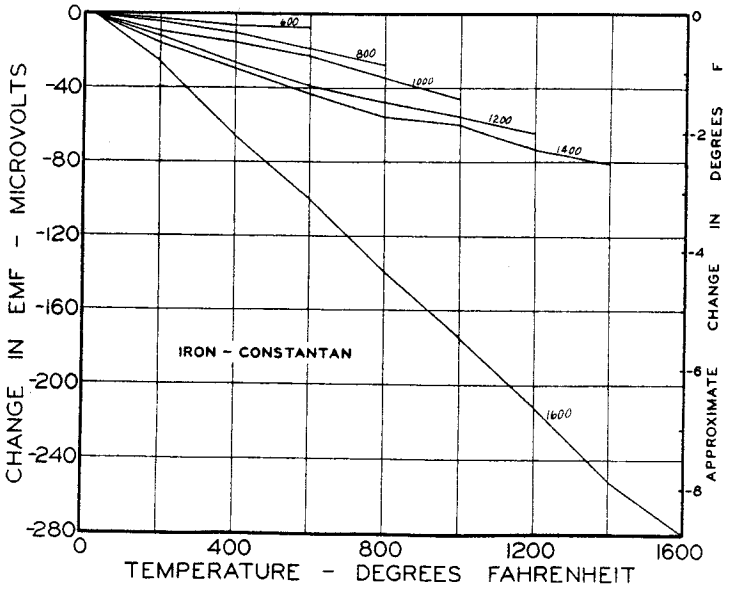

FIG. 19. Changes in the indications of No. 8-gage iron-constantan thermocouples due to a 3-inch decrease in immersion after the couples had been heated for 20 hours in air at the temperatures indicated on the graphs.

From the observations reported it is seen that long-time exposure of a Chromel-Alumel thermocouple to high temperatures causes the emf corresponding to a given temperature to increase, or the temperature corresponding to a given emf to decrease. The effect on an iron-constantan thermocouple is just the reverse.

Failure of a Chromel-Alumel thermocouple (No. 8-gage) occurred within the 1000-hour heating period only in the test at 2200 °F. In this case an open circuit was indicated after 300 hours, and examination of the sample showed that the metal forming the welded junction and the individual wires for some distance from the welded junction were oxidized nearly through.

The 1000-hour heating periods at 2000 and 1800 °F for No. 8-gage Chromel P and Alumel also produced appreciable oxidation of the materials. In the test at 2000 °F the diameter of the wires after the oxide was removed was 2.3 mm for the Alumel and 2.6 mm for the Chromel P, as compared to 3.3 mm for the original diameters. For the test at 1800 °F the diameter after removing the oxide was 2.6 mm for the Alumel and 3.1 mm for the Chromel P. In the tests at 1600 °F and below the oxidation had not materially decreased the diameter of the wires.

Table 2. Changes (in microvolts) at Various Temperatures Caused by Decreasing the Depth of Immersion Three Inches after Heating in Air at the Temperatures Indicated for 20 Hours.

Calibration Temp. (°F)	Heating Temperature (°F) 600	800	1000	1200	1400	1600	1800	2000	2200
				Chromel P					
200	2	4	5	12	10	13	− 1	− 7	− 7
400	5	9	8	21	25	24	+ 1	−12	− 35
600	10	18	19	31	35	36	4	−14	− 50
800		31	30	36	45	45	10	−16	− 49
1000			40	41	54	57	13	−21	− 52
1200				49	59	71	31	−32	− 53
1400					65	79	48	−28	− 81
1600						86	68	−29	−103
1800							95	−28	−130
2000								−18	−158
2200									−176
				Alumel					
200	1	1	2	− 2	− 2	− 3	− 5	−13	− 31
400	3	2	1	− 3	− 4	− 6	−26	−59	−128
600	9	7	− 1	− 6	− 6	− 8	−35	−89	−193
800		10	− 4	−12	−11	− 9	−25	−73	−159
1000			+ 1	−17	−17	−10	−10	−46	−134
1200				−17	−25	−12	−13	−33	− 78
1400					−25	−15	−21	−39	− 86
1600						−17	−32	−54	−110
1800							−45	−74	−157
2000								−102	−214
2200									−281
				Chromel-Alumel					
200	1	3	3	14	12	16	4	6	24
400	2	7	7	24	29	30	27	47	93
600	1	11	20	37	41	44	39	75	140
800		21	34	48	55	54	35	57	110
1000			41	58	71	67	23	25	82
1200				66	84	83	43	1	25
1400					90	94	69	11	5
1600						103	100	25	7
1800							140	46	27
2000								84	56
2200									105

The exposure tests on No. 8-gage iron-constantan thermocouples showed failure of the materials within the 1000-hour heating time for the tests at 1600 °F and above. Failure occurred after 12 hours at 2000 °F, after 28 hours at 1800 °F, and after 300 hours at 1600 °F. The No. 18-gage iron-constantan thermocouple failed after about 500 hours at 1400 °F, whereas the No. 8-gage thermocouple remained serviceable throughout the 1000-hour test at 1400 °F. However, at the conclusion of the test, the diameter of the No. 8-gage materials had been reduced to about 1/10 of their original value.

A summary of the changes observed for Chromel-Alumel, iron-constantan, and Chromel-constantan thermocouples produced by long-time exposure to various temperatures is given in Table 3. The values for Chromel-constantan were obtained indirectly by combining the changes in the individual elements. Though the changes in both Chromel P and constantan are considerably larger than those of the completed thermocouple, the direction is such that the changes counteract

each other, so that the change in a Chromel-constantan thermocouple is small. The life of this thermocouple is limited by that of the constantan element.

The relatively large changes in calibration which were observed for Chromel-Alumel thermocouples at 400 and 600 °F after the couples have been exposed to temperatures of 1600 °F and above are not as serious as may at first appear. When

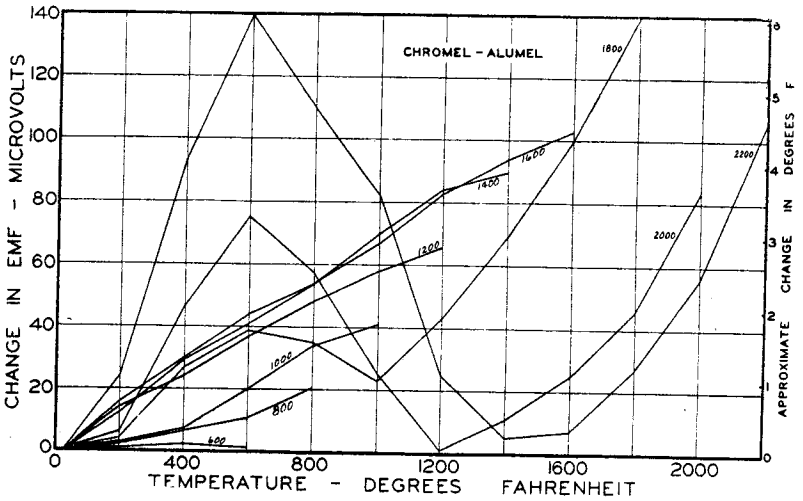

FIG. 20. Changes in the indications of No. 8-gage Chromel-Alumel thermocouples due to a 3-inch decrease in immersion after the couples had been heated in air for 20 hours at the temperatures indicated on the graphs.

a thermocouple is used for accurate measurement of temperatures of 1600 °F or above it is seldom required that this same couple be used for accurate measurement at temperatures as low as 400 or 600 °F. Therefore the relatively large changes at these lower temperatures are of no great importance. A thermocouple which is to be used for accurate measurements below 1000 °F should not be exposed to the higher temperatures. If this procedure is followed the relatively large changes at 400 and 600 °F will be avoided.

Table 3. Changes in the Calibration of Base-metal Thermocouples Heated in Air (Electric Furnace).

Exposure Temp. (°F)	Chromel-Alumel Exposure (hrs)	Chromel-Alumel Maximum Change (°F)	Iron-Constantan Exposure (hrs)	Iron-Constantan Maximum Change (°F)	Chromel-Constantan Exposure (hrs)	Chromel-Constantan Maximum Change (°F)
800	1000	< 1	1000	< 1	1000	<1
1000	1000	< 1	1000	< 1	1000	<1
1200	1000	+ 2	1000	− 4	1000	− 1
1400	1000	3	800	− 7	1000	− 2
1600	1000	5	100	−10	100	− 4
1800	1000	8	28	−18		
2000	1000	19	8	−19		
2200	200	21	....	....		

The results on the immersion tests emphasize the importance of never decreasing the depth of immersion of a thermocouple after it has once been placed in service. The practice of using a single base-metal thermocouple for high-temper-

ature measurements in a number of different installations should be avoided. It is even difficult to obtain consistent and accurate results by using a thermocouple in a single installation if the couple is withdrawn and replaced between periods of service. The results obtained by removing a used base-metal couple from an installation to determine the corrections to the original calibration by testing it in a laboratory furnace are unreliable. The temperature gradients in the two furnaces usually differ widely, and hence the results will not be applicable to the actual service conditions. If it is practicable by any means to remove the inhomogeneous portions of the thermocouple from the temperature gradient, then the original calibration of the couple is applicable.

Discussion

W. A. Gatward, Chief Engineer, Hoskins Manufacturing Co., Detroit, Michigan: Mr. Dahl has very carefully limited his statements regarding this experiment to cover oxidizing conditions only. He has found under such conditions that generally, Chromel-Alumel thermocouples will produce higher emfs after use. In practice it is usually found that the opposite is true, that is, that when changes develop, the couples usually "read low." The tendency to read low will be caused by reducing gases which are likely to be present even under the best protection. We might say then, that the tendency to read high as caused by oxidation will in many instances be partially, wholly, or excessively compensated by the tendency to read low, as caused by gas contamination.

Mr. Dahl is dealing with very small changes, some of them equivalent to fractions of a degree. There are some instances where the data are not consistent, as for instance where he gets more change in 100 hours than in 200 hours, or where his curves cross over. I know when trying for such accuracy as this, that errors are apt to creep in, and there are two questions I would like to raise concerning his technic.

Asbestos wool was used to plug up the end of the test furnace. That has been known to cause errors if a reducing gas is driven off from the wool and into the furnace at a high enough temperature. The exact limitations of the use of asbestos wool are not known, so it should be used with caution.

The other point involves temperature gradients. With the test wires and the platinum couple all welded together it is possible to take perfectly good readings while the temperature is changing. However, the effect of the temperature gradient is such that plenty of time should be allowed for the temperature gradient to reach its equilibrium. For a given design of furnace there will be a very different temperature gradient for each temperature used, and it takes considerable time for this gradient to establish itself. Too rapid manipulation of the temperature of the furnace is suggested as a possible cause of some small discrepancies.

Possibly the accuracy of the potentiometer is not consistent with the accuracy of the control of conditions in the test and part of the data may be out of "accuracy balance."

It is quite evident that temperature gradient, a necessary evil, is one of the important considerations in the use of thermocouples. Very few people are familiar with what goes on in the "zone of uneven heating" or, the "temperature gradient," and I believe a more thorough discussion of the problem would be in order in this paper.

In discussions of this sort we use terms which we would be hard-put to define. For instance, inhomogeneity. Now we have a pretty good conception of its opposite, homogeneity, because a piece of wire is homogeneous if a temperature gradient does not set up local emfs or "parasitic emfs." It is pretty safe to say that such a wire is very uniform as to composition and physical state.

If a wire is such that parasitic emfs *are* set up by a temperature gradient, then we say that it is inhomogeneous without knowing wherein inhomogeneity lies. Maybe the hottest part of the wire has lost some small part of its chemical ingredients. Maybe some surface oxide has been reduced permanently or temporarily. Maybe the physical state or the crystal form (as in the case of nickel) has been temporarily or permanently disturbed so that a parasitic emf could "come and go," depending on the temperature at the moment.

These are mentioned just as possibilities, to show that inhomogeneity may be one or several things all at the same time. Whatever it may actually be, it is the temperature gradient acting on the non-uniform wire which causes parasitic emfs which add or detract from the total couple emf.

It is one thing to age a couple wire when we heat the whole wire to some high temperature, as for annealing or stabilizing purposes. But aside from that, each couple in use is submitted to an ageing process, not at one temperature but at many temperatures along its length. A couple must reach from the high-temperature zone out to room temperature and it must pass through a temperature gradient. Hence, the couple in use is not aged uniformly at all.

Notice that in Mr. Dahl's curves, Figs. 1 to 4 inclusive, where the ageing temperature only reaches 1400 °F, the changes are more or less uniform and proportional to time and temperature. Those in Figs. 5 to 8 inclusive are quite different with decided "humps" in the Alumel curves at 400 to 500 °F.

It must be borne in mind that a couple which is aged at 1400 °F must pass through a continuous gradient clear to room temperature just as does the couple which is aged at 1600 °F. And still the couple aged at 1600 °F will exhibit the "hump" at 400 to 500 °F while the one aged at 1400 °F will show no "hump."

It is hard to believe that a hot-end temperature of 1600 °F would *in itself* cause an effect different from 1400 °F. It is pretty certain that if two wires were completely aged (the whole length) at 1400 and 1600 °F they would behave in the same way as to the hump. Knowing the peculiarities of nickel at 400 to 500° F, and knowing that Alumel is 95 per cent nickel, we would expect that the hump in the Alumel curve must be caused by a temperature at around 400 to 500 °F, which can only occur in the temperature gradient.

Fig. 21 has been drawn to represent a possible temperature distribution in a test furnace. Curve A could be the temperature of a wire being aged at 2000 °F. It will have one end in a uniform zone, L_5, and the other end at room temperature L_1. The remaining part represented by L_2, L_3, and L_4 will be in the gradient zone. Now forget L_2 and L_4 for a moment and think of L_3 as representing the inhomogeneous wire which has been aged at many different temperatures along its length. One end could be at 1500 °F, and the other end could be at 500 °F. If L_3 is inhomogeneous then 1500° at one end and 500° at the other end would cause a parasitic emf, and it might add to or it might subtract from the emf of the whole wire against platinum.

Now after the aging at 2000 °F, suppose the temperature of L_5 is dropped to B, or to 500 °F. We know that the two ends of L_3 will also be lowered say to 400 and 200 °F, and any parasitic emf, if present, will be of different degree and might even be of different sign.

Isolating L_3 and making the foregoing assumptions, we can see that the temperatures involved could be those which would affect the Alumel. While this is all speculation and does not suggest any cure for the effect of a temperature gradient, it does suggest an experiment which might explain the hump.

A furnace could be made up with 3 controllable zones, one representing the section L_5 and the two others which could be controlled at lower temperatures and which would represent the two ends of L_3. Then a length of wire could be welded into the Alumel wire, an insert several inches long, and of material having a decidedly different emf from the Alumel wire. This insert would then represent L_3.

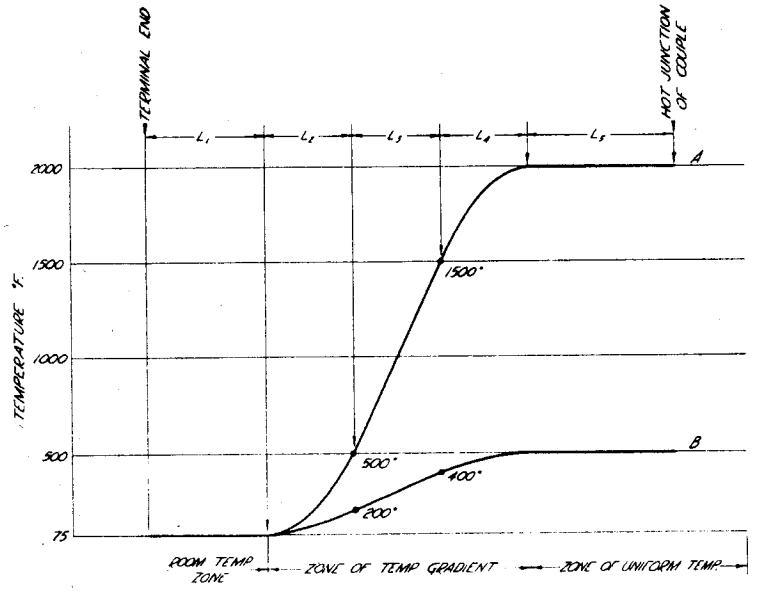

FIG. 21. Possible temperature distribution in test furnace.

Now a test could be run with selected temperatures for the ends of L_3 and a selected temperature for L_5. Then L_5 could be changed, but the difference in temperatures at the ends of L_3 could be kept the same, so that any parasitic emf in L_3 would be the same regardless of the temperature of L_5. This sort of experiment would contribute something to the explanation of the hump in the Alumel curves.

Time Rate of Change When a Chromel-Alumel Couple is Not Disturbed and is Held at One Temperature

When accurate temperatures must be measured over a long time, the couple should be checked periodically "in place," that is, not disturbed in any way. There are data in Figs. 1 to 8 inclusive which will tell what to expect in changes of emf with time. These data can be taken from Figs. 1 to 8 at the extreme right-hand end of the curves. Fig. 22 has been prepared in this manner. In some cases the curves cross over and it is not possible to identify all of them. When this occurs, the average of the group is used. It occurs only where the changes are very small, a degree or so.

Mr. Dahl's paper may at first be alarming to users of Chromel-Alumel couples. Many of them depend implicitly on check couples which are used at many temperatures and immersions.

In discussing the use of couples the expected accuracy should always be stated

so that a user may decide just how he may operate his couples to attain the desired accuracy.

Mr. Dahl has carefully defined the conditions of his experiments as oxidizing. He has made some valuable suggestions in the use of Chromel-Alumel couples. However, it seems if he could combine his recommendations with his statements defining the accuracy expected, then his recommendations would have more practical use. If such accuracy cannot be conveniently defined, then he might head his list of recommendations with the statement that "extreme accuracy requires the following precautions." Such precautions selected from various paragraphs could then be summarized as follows.

(1) A couple which is used for measurements below 1000 °F should not be exposed to higher temperatures.

(2) A Chromel-Alumel couple which is used up to 1600 °F or higher should not be used for accurate measurements below 800 °F.

(3) The depth of immersion should not be changed from the original, and above all it should not be decreased.

(4) Any thermocouple should be checked if possible in place, *i.e.*, undisturbed in any way.

Reply

The asbestos wool used to close the ends of the furnace tube did not become heated to temperatures sufficiently high to disturb the oxidizing atmosphere within the tube. The wool was loosely placed against the ends of the tube. This permitted a relatively easy passage of air into the tube and if any foreign gases were

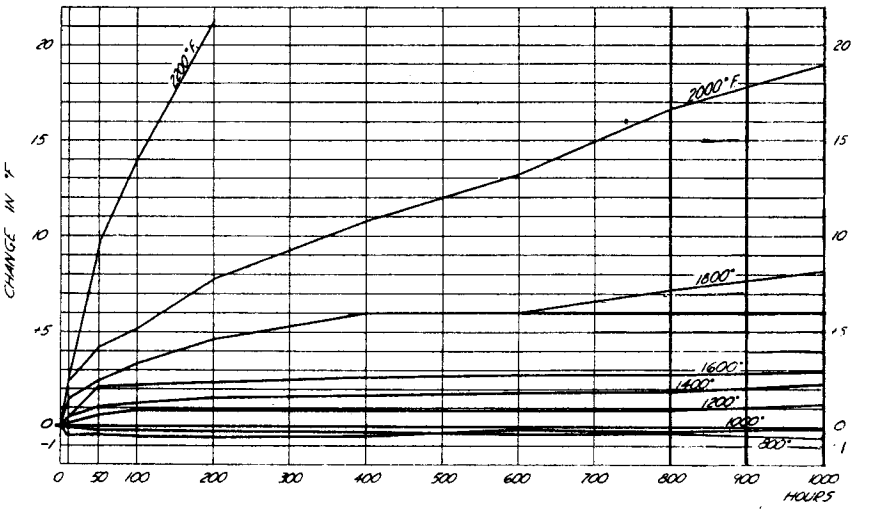

FIG. 22. Rate of change for Chromel-Alumel couples left undisturbed and aged at temperatures shown.

liberated from the asbestos wool they would be so diluted with an excess of air that their effect would be negligible.

The time allowed for the temperature gradients in the test wires to become established after the furnace reached the desired steady temperature was about 15 minutes for temperatures up to 1200 °F and about 10 minutes for temperatures

above 1200 °F. Moreover, the furnace temperature was changed slowly in passing from one point to the next. The emf of the test wires against platinum at the time the observations were recorded showed no variation with time when the temperature was maintained constant. This would indicate that equilibrium conditions had been reached.

The over-all accuracy of the measurements at any given temperature, including the uncertainties in the potentiometers, the standard thermocouple, and the platinum reference wire, is estimated to be within 0.5 °F.

Discussion

A. H. Salerno, Hyatt Bearings Division, General Motors Corporation, Harrison, N. J.: Commenting on Mr. Dahl's paper from the viewpoint of the pyrometer user, I wish to say that in the selection of the type of material to be used for base-metal thermocouples in commercial application, it is necessary to know the conditions under which the wire will be used. Characteristics are influenced by type of atmosphere, whether oxidizing, neutral or reducing, and by time and temperature. Having decided upon the particular conditions, it is of extreme importance to consider the economies involved. It is well known that different types of couples will have a variable life depending upon the amosphere in which they are used. The comparative cost per hour of service might justify the use of the less expensive of two wires, even though it is necessary to change couples more frequently. The fact that a couple must be taken out of service to avoid errors with continued use before failure occurs does not necessarily indicate an unsatisfactory type of material. Frequency of changing couples can be adjusted to avoid using them beyond the point of instability.

The atmospheric conditions encountered in the tests reported on by the author were undoubtedly quite strongly oxidizing. This condition is not always met with in practice.

In cases where difficulties might arise from using couples in a strongly oxidizing atmosphere, it is often advantageous to pack them so as to exclude as much oxygen as possible and thereby lengthen their service life.

Our practice in the use of iron-constantan thermocouples is to replace with new couples at regular stated intervals, regardless of their apparent condition. The length of time allowed in service depends on the temperature of operation. This is given below for I-C couples.

Temperature of Use	Period of Use
1700 °F	672 hours
1450–1550 °F	360 hours
300–800 °F	8760 hours

These periods are for 24 hours per day, 7 days per week. The 1700 °F-couples are packed with T.C. packing, while the others are in unpacked tubes. This accounts for the apparent discrepancy between the 1700 °F and the 1450-1550 °F time of use figures. The time of service does not indicate failure but has a large factor of safety, since the couples are inexpensive and the parts being heat-treated are valuable.

Since we have never made life tests on any thermocouple wire we are not in a position to offer comments on the stability under these conditions, other than the data given above.

G. C. Stauffer, Driver-Harris Co., Harrison, N. J.: The author of this paper should be complimented on the work done with the very desirable object of collecting information on the life of base-metal thermocouple materials.

Attention should be called to the fact that the results in this paper indicate the effect of definitely oxidizing conditions on base-metal thermocouple elements. It appears quite probable that the test conditions were considerably more strongly oxidizing than is met with in the industrial applications of base-metal thermocouples.

The results on constantan indicate what happens when it is exposed to an unknown concentration of oxygen at elevated temperatures for various periods of time. The heretofore unpublished data below indicates that the oxygen concentration in the atmosphere is more significant than the time factor. The life of any couple depends on the atmosphere. Strongly oxidizing atmospheres on an unprotected iron-constantan couple will cause rapid deterioration at temperatures over 1600 °F. It is well known that reducing atmospheres are equally destructive to some other types of base-metal couples.

In 1934 the National Bureau of Standards made some routine commercial calibrations against platinum of keyed samples submitted by the alloy manufacturer. Nine samples from one coil of No. 8 wire were taken. The coil had been given a commercial anneal at 1450 °F for 4½ hours in a closed pot. A neutral or slightly reducing atmosphere was maintained.

Of the nine pieces, one sample received no additional heat treatment. Four of the remaining samples were heated for three hours in pure hydrogen, the other four were placed in steel tubes packed with Aloxite and sealed on the ends with fireclay. This was termed an oxidizing anneal. The eight samples were then heated for three hours to the temperatures indicated.

Table 4. Heat Treatment.

Sample Number	Time (hrs)	Temp. (°F)	Atmosphere	Emf vs. Pt 27 at 1500 °F (mv)	Net Change from No. 1 (μv)
1	.	....	.....	35.53	00
2	3	1400	Hydrogen	35.55	− 20
3	3	1600	Hydrogen	35.58	− 50
4	3	1800	Hydrogen	35.60	− 70
5	3	2000	Hydrogen	35.59	− 60
6	3	1400	Oxidizing	35.47	+ 60
7	3	1600	Oxidizing	35.52	+ 10
8	3	1800	Oxidizing	35.03	+500
9	3	2000	Oxidizing	34.97	+560

It would be expected that, if the oxidizing conditions were uniform for samples No. 6 and No. 9 inclusive, the change in microvolts would be consecutively greater with higher temperatures of treatment. It should be noted that this is not the case, which indicates that the oxidizing conditions were not uniform.

Comparing the tests in oxidizing atmospheres given in Table 4 with the figures given by Mr. Dahl, it will be seen that Sample No. 6, for example, shows a greater change than is given by Mr. Dahl in Fig. 14 for the same temperature but a longer period. The change on sample 7 for the oxidizing atmosphere at 1600 °F compares approximately with the data given by Mr. Dahl in Fig. 15.

A recent test to show the effect of exposure of constantan to severe oxidizing conditions for three hours at 1700 °F showed a change of 1650 microvolts when checked at a temperature of 1500 °F.

The results on the samples in the reducing atmospheres all having increased slightly, it is logical to assume that a strictly neutral atmosphere would have caused

no change. Thus variations in atmospheric oxygen content will cause changes as high as 1650 microvolts at a 1500 °F test temperature when the wire is heated for only three hours. This indicates the necessity of knowing the condition of oxidation of the atmosphere in contact with the couple.

Commercial practice has indicated throughout the years that properly installed couples do not deteriorate at the rate shown by Mr. Dahl. Actual values fall between the ideal of no change, in the reducing atmosphere, and the rapid change shown under oxidizing conditions.

The amount of increase in emf after heating in reducing atmospheres has been determined to depend on the previous history of the sample. Properly melted and annealed samples show only slight changes. A piece which has been severely oxidized may be restored to its original value by heating in hydrogen at a temperature of 1850 °F for from 15 minutes to an hour or more. For example, the previously mentioned piece which changed 1650 microvolts after heating for 3 hours at 1700 °F in an oxidizing atmosphere and which had scaled off 0.005″ was fired for one hour at 1820 °F in an atmosphere of pure hydrogen.

Original value	35,500 μv vs Pt 27 at 1500 °F
After oxidizing at 1700 °F	33,850 μv vs Pt 27 at 1500 °F
After hydrogen heating at 1820 °F	35,575 μv vs Pt 27 at 1500 °F

The change is not due to the reduction of the surface oxide, since if the surface is completely removed by pickling or machining, the emf of the wire does not return to the original value until it has been fired in hydrogen.

It is apparent from this that the core of the metal in some way takes up oxygen, which definitely lower the emf of the wire. This effect on the emf is neutralized, and the oxygen is presumably removed when the wire is heated at high temperatures in an atmosphere of hydrogen.

It is obvious from the foregoing that when iron-constantan thermocouples are used it is desirable to use tight protection tubes and limit infiltration of air to the minimum.

Reply

I do not agree with Mr. Stauffer's statement that "the results on constantan indicate what happens when it is exposed to an unknown concentration of oxygen at elevated temperatures for various periods of time," because the atmosphere in which the materials were heated was that of clean air and therefore of known and constant oxygen content. The rate at which oxygen was consumed in the oxidation of the materials during heating was not great enough to change the oxygen concentration within the furnace appreciably since an excess of air was present at all times.

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2. Burgess, G. K., *Bur. Standards J. Research,* 1, 635 (1928) (RP 22).